

# Selenium Leaching Kinetics and In situ Control

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**Abstract** Selenium leached from coal tailings and spoil is a challenge for mining operations in southern West Virginia. Selenium discharges are not supposed to exceed 5 µg/L, and yet are commonly in the range of 10–25 µg/L. Once in the selenate form, selenium removal can be extremely difficult and expensive, particularly in the narrow valleys and highly variable flow regimes of southern West Virginia. This study reports on the first 96 weeks of a leaching study. Selenium leached at the rate of 0.06% of the extant selenium pool per day. After 96 weeks, about 35% of the original, potentially mobile selenium had leached. While sulfur was far more abundant, its leach rate was about 10% of the selenium rate. Iron oxyhydroxide was found to reduce the concentration of dissolved selenium by about 70%, which indicates that selenite is the dominant, mobile selenium species during initial weathering, and that selenium could be controlled at its source, through special handling and treatment of selenium-rich rock units. Iron oxyhydroxide kept selenium near the regulatory limit of 5 µg/L throughout the experiment.

**Keywords** Coal tailings · Selenium · Sulfur kinetics · In situ control

## Introduction

Coal mine drainage in West Virginia falls into two general categories, acidic drainage from pyrite-rich coal seams, usually found in northern WV, and neutral drainage from low-sulfur southern West Virginia coal seams. In the United States, selenium is subject to several regulatory limits: 50 µg/L (US EPA primary drinking water), 20 µg/L (acute aquatic life toxicity), and 5 µg/L (chronic aquatic life toxicity). The 5 µg/L value is the selenium discharge limit for coal mines in West Virginia. Although rock from both regions contains selenium, the northern, typically, acidic mine drainage contains little if any selenium, whereas the southern neutral drainage is potentially subject to regulatory action due to selenium levels of 10–25 µg/L. Selenium discharges were only recently recognized as an environmental issue in the region, so previously, there was no attempt to identify or isolate selenium-bearing rock units during mining. As a result, many discharges from southern West Virginia surface mines and tailings facilities now require treatment. (Tailings are the rock and other residuals that are removed during the coal cleaning process.) Current mining operations seek to identify selenium-rich rock layers, and then treat or isolate them to avoid future selenium releases into the environment. Thus, the selenium problem has two aspects, development of methods to treat selenium-rich discharges from existing facilities and development of a materials handling strategy to prevent selenium discharges from newly generated waste rock.

Given the technical and financial burdens of treating selenium discharges, controlling selenium at the source is an attractive option. Such treatment requires understanding: (1) the proportion of selenium that is potentially mobile; (2) the kinetics of its release; (3) identification of

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in situ treatment methods; (4) application rates, and; (5) long-term performance at operational scale. This paper discusses early steps undertaken to address items 2, 3 and 4. Specifically, southern WV coal tailings were studied with respect to selenium release and the effectiveness of in-place treatment with iron oxyhydroxide.

Earlier evaluations (Coleman et al. 1993; Mullenex 2005) of coal and coal overburden in Southern West Virginia indicated concentration of selenium-enriched rock primarily in the vicinity of the coal seams. Work performed by Roy (2005) and Vesper et al. (2008) demonstrated that selenium found associated with the coal seams, organic shale, and other carbon-rich zones contain levels of selenium that may be problematic if allowed to freely leach into mine discharge.

The natural rate of selenium release from sedimentary rock has not been widely studied. The studies of Roy (2005) and Pumure et al. (2010) used extreme methods to stimulate selenium release from rock. Roy (2005) showed that roughly one half of the total selenium present in rock samples from southern West Virginia was non-extractable under severe chemical attack while another quarter of the total selenium was bound in organic form. Neither of these selenium forms was shown to contribute significantly to the mobile fraction. Most of the remaining selenium that could be potentially mobile in the environment occurred in association with sulfides and, to a lesser extent, as exchangeable ions. Thus, only about 25–35% of the total selenium revealed by total overburden analysis was found to be mobile. Selenium occurs at extremely low concentrations in non-carboniferous sandstone and shale units and these units do not appear to be responsible for elevated levels of selenium in mine discharges.

Similar results were obtained using a sonication extraction intended to estimate bioavailable or mobile selenium (Pumure et al. 2010) in shale. Samples were sonicated in deionized water for 90 min in 5 min increments with total replacement of the water for each 5 min extraction. The authors reported that 35 and 38% of total selenium in two similar organic shales from southern West Virginia was mobile. In theory, sonication enhanced the oxidation of reduced selenium forms via cavitation and released soluble selenium. The predominant form of selenium (selenite or selenate) was rock-dependent.

Diehl et al. (2005) found selenium in pyrite studied in southern Appalachian coals by a variety of microanalytical techniques. Up to 670 mg/kg of selenium was found in the pyrite samples. The minimum sulfur to selenium ratios in their pyrite samples were close to  $10^3$ . Whole coal values for selenium ranged from 25 to 247 mg/kg. At 1–2% sulfur content (estimated, sulfur content was not reported), the pyrite contained roughly 2–20% of the selenium in the coal. The selenium percentage found in pyrite correlates

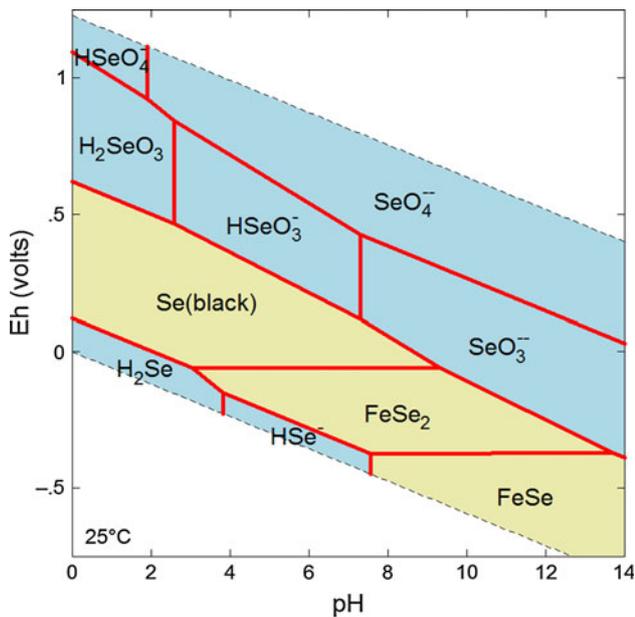
well with the fraction found in the sulfidic extract by Roy (2005), who found 8% of the total selenium in the pyrite fraction for coal and 13% for shale. Diehl et al. (2005) concluded that trace element enrichment was post-depositional to pyrite formation.

Selenium in waste rock can exist in soluble forms, such as selenite or selenate, which will be released immediately upon exposure to water, or in solid forms that become mobile upon exposure to oxygen and water. Very little is known about the actual selenium forms in rock. The concentration of selenium is too low for determinations by all but the most sophisticated analytical equipment, but the most commonly presumed species is the selenium analog of pyrite. The Pourbaix diagram for iron-selenium (Fig. 1) shows areas of thermodynamic stability for elemental selenium, in addition to more reduced iron-compound forms. In natural systems, ferroselite ( $\text{FeSe}_2$ ), ferrous selenide ( $\text{FeSe}$ ), and/or elemental selenium ( $\text{Se}^0$ ) may comprise the dominant solid form. The differences in the oxidation mechanisms and kinetics for these solids are unknown. Figure 1 also shows that with increasing oxidation potential ( $E_H$ ), the first stable soluble species is selenite ( $\text{SeO}_3^{2-}$ ) and its protonated forms. The oxidation of selenite to selenate is slow. As an example, Vesper et al. (2004) showed that the proportion of selenate to selenite gradually increased downstream of coal mines, indicating both initial release of selenite and slow oxidation. Selenite is often the primary species found in various power plant ash materials (Huggins et al. 2007), although Hyun et al. (2006) found significant selenate. Our presumption is that newly oxidized rock, regardless of the solid selenium form, will release selenite.

Selenite is known to bond more strongly to solid surfaces than selenate (Elrashidi et al. 1987, 1989) due to inner-sphere complexation (Zhang and Sparks 1990). Twidwell et al. (2000) cited an iron hydroxide precipitation/adsorption method as the EPA best available technology for selenite removal, stating that the technology is unsuitable for selenate. They noted the influence of interfering ions, equating the removal efficiency of selenate inversely to sulfate concentration. The effluent selenium concentration from a pilot facility using ferric hydroxide precipitation was 10  $\mu\text{g/L}$ , which would not meet the 5  $\mu\text{g/L}$  USEPA discharge limits.

An earlier, extensive engineering study conducted by the Electric Power Research Institute (EPRI) (Merrill et al. 1985) evaluated selenium removal using iron hydroxide, but the study was focused on higher concentrations of selenium (400–800  $\mu\text{g/L}$  in coal ash ponds) than found in coal mine drainages (<50  $\mu\text{g/L}$ ).

Two methods, adsorption and co-precipitation can be used to remove trace metals with ferric oxyhydroxides, which is the preferred term in this instance due to the large



**Fig. 1** Aqueous Pourbaix diagram of  $10^{-6}$  M (79  $\mu\text{g/L}$ ) selenium and  $10^{-3}$  M (56 mg/L) iron species at standard temperature and pressure. Solid forms are indicated by buff shading. Soluble species are indicated by blue shading

number of possible solid forms to be found when mixing ferric ion and hydroxide. Introduction of dispersed solid iron oxyhydroxide form led to adsorption of dissolved selenium species onto the solid particles. Merrill et al. (1985) found that roughly 95% of selenate was removed from solution at pH 4, which decreased to less than 10% at pH 7. A more recent study (Anonymous 2007) also noted that selenate is removed below pH 4 when using the ferric oxyhydroxide method.

Iron oxyhydroxide removed 95% or better of the selenite at pH 4 (Merrill et al. 1985). Removal decreased to 80% at pH 9, and decreased further above pH 9. That study used a total iron concentration of 56 mg/L. The authors stated that selenium removal was independent of the iron process used; co-precipitation and adsorption onto preformed solids were equivalent. Merrill et al. (1985) concluded that selenium could be removed across a broad pH range as long as the predominant form was selenite. Also noted was the ability of sulfate to compete for adsorption sites with selenate, thereby suppressing selenate removal. This is germane to West Virginia coal settings where sulfate in discharge water is typically in the range of 500–1,200 mg/L.

Subsequent to the EPRI work, a number of scientific studies focused on selenium adsorption. Su and Suarez (2001) used optical methods and concluded that both selenite and selenate formed inner sphere complexes. They studied amorphous iron oxide and goethite,  $\alpha\text{-FeOOH}$ , and reached similar conclusions for each material, although the

data for amorphous iron oxide were less definitive. Zhang and Sparks (1990) had previously studied selenate and selenite on goethite using a pressure jump relaxation method and, unlike Su and Suarez (2001), concluded that whereas selenite formed an inner sphere complex, selenate formed a less stable outer sphere complex.

Other adsorbents, such as alumina, have proven to be less satisfactory than ferric hydroxide. Twidwell et al. (2000) cited a ferric hydroxide/peat/resin method that showed promise. The peat presumably aids in the reduction of selenate to selenite. Selenite and selenate immobilization by cement materials is also attributed to adsorption (Baur and Johnson 2003).

## Experimental

### Design

The project was a completely randomized analysis of variance with six replications per treatment combination (Ostle 1963). Treatments included control (no FeOOH) and FeOOH treated cells. The time variable included measurements taken during the 96 week leaching period. Parameters of interest were elemental leaching rate (percent of original selenium or sulfur leached). Four separate two-factor analyses of variance were run to evaluate the effect of time on elemental leaching rate independent of treatment then the effect of treatment on each element's leaching rate. The null hypotheses held that there would be no significant differences in leaching rates as functions of treatment, element, time or their interactions.

### Materials

Our long term study used coal tailings from southern West Virginia. These tailings generate selenium but do not generate acid from pyrite due to concomitant alkalinity. In this study, the coarse tailings fraction was used. It was collected from the belt line exiting a coal preparation plant in southern West Virginia. This material is produced with a nominal size range between 0.075 and 11 mm. The material was screened to exclude rocks larger than 1.25 cm. Most of the rock that reports to the tailings pile is a mixture of coal and organic shale partings. Quaranta and Tolikonda (2010) summarized the typical particle size distribution of southern West Virginia coarse coal tailings and found 93% to be below 11 mm in diameter (coarse gravel to fine sand). Forty three percent of the particles were larger than 1 mm.

The iron oxyhydroxide treatment material was supplied by Hedin Environmental Services (Pittsburgh, PA). The material was harvested from an aerobic wetland where the influent water contained sufficient alkalinity (bicarbonate)

to maintain neutral conditions. The iron oxyhydroxide was produced by passive oxidation and settlement of the floc.

## Methods

Solids samples were analyzed for total selenium by complete acid digestion followed by hydride generation atomic fluorescence spectroscopy. Analyses were conducted by REIC Laboratories in Beaver, WV.

Twelve treatment cells were constructed for the southern WV tailings. Six cells were untreated controls and six were treated with iron oxyhydroxide. The iron oxyhydroxide application (14.7% dry weight basis) was blended with approximately 515 g of coal tailings. After initial leaching, these cells were placed on 1 cm thick spacers, to allow free drainage, inside 2 L plastic containers equipped with removable, sealable lids.

After the initial leaching treatment, cells were sealed, and then leached every 2 weeks thereafter for a period of 33 weeks using the leaching cell, which was placed on top of a 1 L treatment cell containing tailings or treated tailings. After 33 weeks, leaching was conducted every 2 or 4 weeks for a total of 96 weeks. Then, 1 L of deionized water was poured into the top, empty 1 L container. By holding these stacked containers above the empty 2 L container, deionized water was applied evenly to the treatment cells. Leachate was collected in the 2 L container. Half of the leached water (500 mL) was poured into a labeled sampling bottle, measured for pH, and refrigerated pending transportation to the analytical laboratory for determination of acidity, alkalinity, chloride, and sulfate. The remaining 500 mL was filtered through a 0.45 µm membrane filter (Millipore Corporation). The filtered water was collected in a labeled sampling bottle and acidified with nitric acid for determination of Al, Fe, Mn, and Se. All chemical analyses were conducted by REIC analytical laboratories in Beaver, WV. Metals were analyzed by ICAP emission spectroscopy, sulfate and chloride by ion chromatography, and selenium by hydride generation atomic fluorescence spectroscopy.

## Data Analysis

The leachable proportions of selenium in coal and organic shale reported by Roy (2005) were averaged to estimate the residual proportion in the tailings. For the purposes of discussion, an average value for extractable selenium in shale and coal as found by Roy (2005), 33%, will be used here. This value also agrees with the results of Pumure et al. (2010). Application of this percentage yielded an estimated initial value of 26.4 µg (0.0033 mmol) of mobile selenium in each leaching cell.

After processing in the preparation plant, tailings, samples of which were used in this study, are placed in a valley where the discharge is routinely monitored and treated as necessary. The disposal site contains about  $2 \times 10^7$  t of tailings. The concentration of chloride, a conservative ion, leaching out of the pile was 6.4 times greater than that found in the leaching cells. Presumably this accounts for the lower solids/liquid ratio of leaching under field-scale conditions. When this dilution factor of 6.4 was applied to cell leachate concentrations, selenium concentrations from the control leaching cells also fell within the range observed in the field (2–32 µg/L, averaging 12 µg/L). This dilution factor was used with our leaching data in some instances to estimate the selenium concentration likely to occur under field conditions. However, unless otherwise specified, all concentration data are the actual concentrations obtained from the test cells.

Points in many of the figures have been connected by lines to aid visualization. The lines have no predictive function for times between measured points.

## Results and Discussion

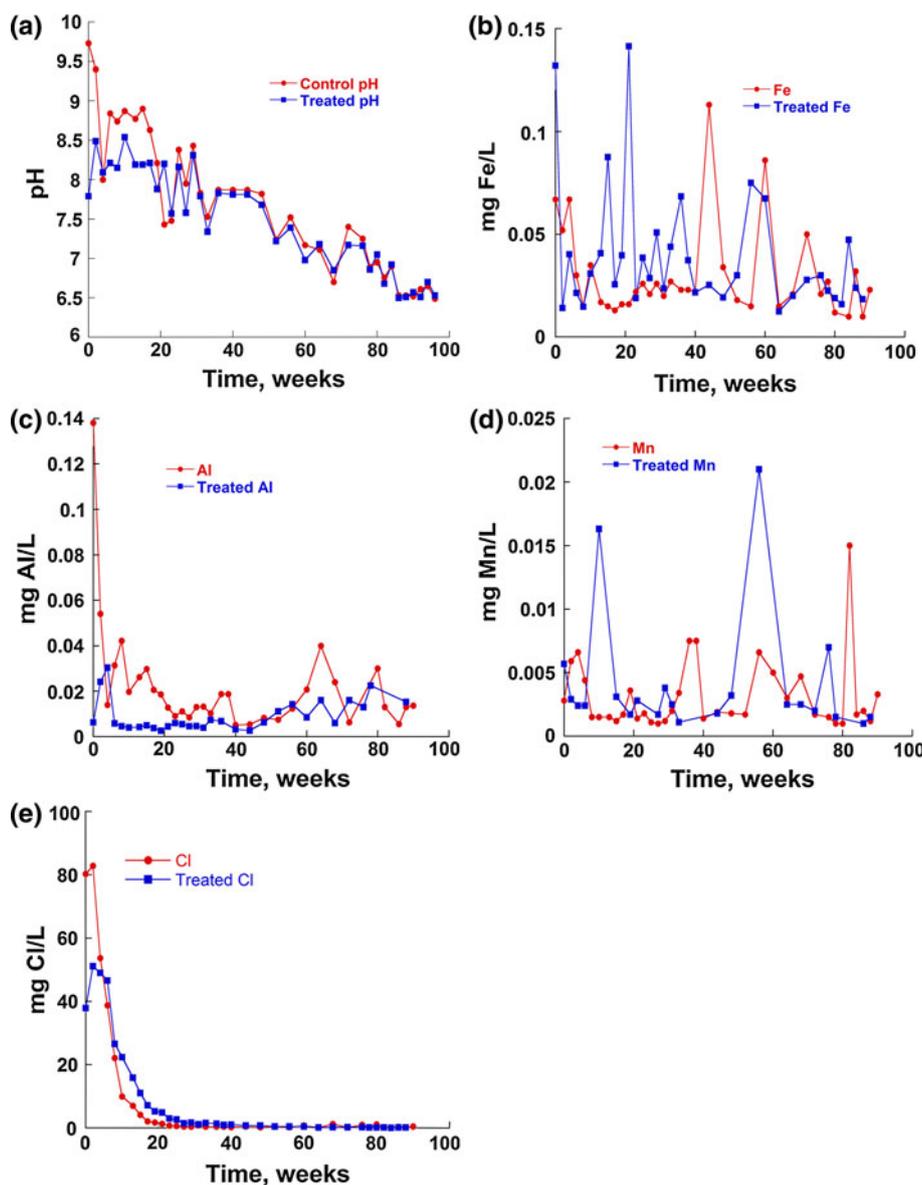
### General

The tailings were characterized (Table 1) and found to contain 1.55 mg/kg of selenium. The sulfur to selenium ratio is 1,200. The release of other measured ancillary species, and pH as a function of time (Fig. 2a, b, c, d, e) provide a full view of the dynamics of the cells. The pH shows a gradual decrease with time due, most likely, to a depletion of the effective alkalinity in the system as more acid is generated. The pH in control cells and treated cells behaves similarly, although the control cells had a higher starting pH. Iron (Fig. 2b) is released at a relatively constant rate for both treated and untreated samples, with occasional concentration spikes. Aluminum (Fig. 2c) is released at higher concentrations by the control early in the experiment, which hints at aluminum control by the iron oxyhydroxides, although no history of using iron to control aluminum exists. Later, the aluminum

**Table 1** Chemical characterization of solid tailings, in mg/kg

Al	2,160
Ca	600
Fe	3,930
Mg	920
Mn	34.7
S	1,850
Se	1.55

**Fig. 2** **a** pH of treated *filled square* and untreated *filled circle* tailings over 96 weeks. **b** Iron released from treated *filled square* and untreated *filled circle* tailings over 90 weeks. **c** Aluminum released from treated *filled square* and untreated *filled circle* tailings over 90 weeks. **d** Manganese released from treated *filled square* and untreated *filled circle* tailings over 90 weeks. **e** Chloride released from treated *filled square* and untreated *filled circle* tailings over 90 weeks

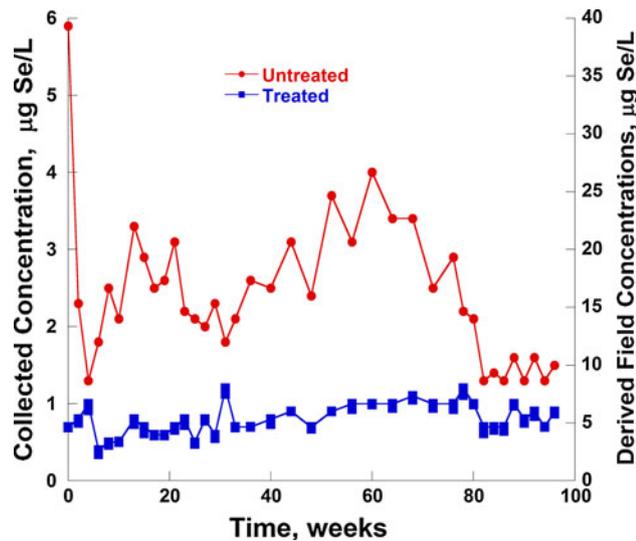


concentration increases for both control and treated cells, which coincides with the pH decrease. Manganese (Fig. 2d) maintains a constant discharge concentration, with an occasional concentration spike. No difference between treated and untreated cells is obvious. Chloride decreases from initially high values in both treated and untreated cells. The untreated cells have a higher concentration of chloride at early times, but the concentration falls off more quickly than for the treated cells. Control rock released 6% more chloride (0.32 g) than the treated material (0.30 g) Chloride does not have concentration spikes and behaves like an ion that has a finite initial concentration that is flushed and not replenished to any appreciable extent by rock oxidation.

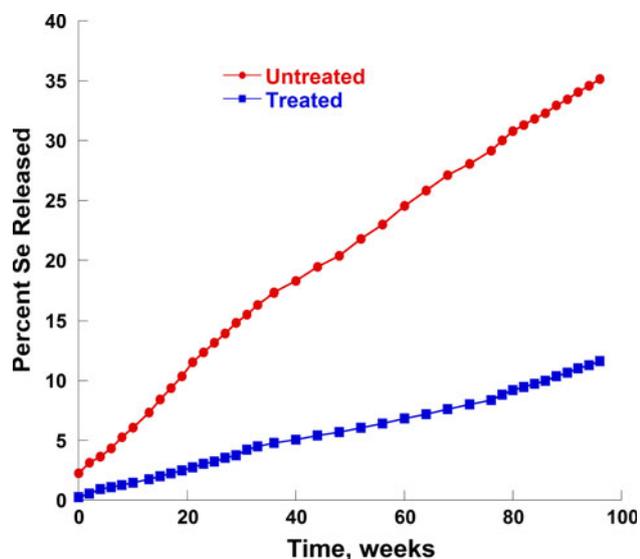
Selenium

The leaching of selenium (Figs. 3, 4) over the 96 weeks shows diminished release of selenium in the presence of iron oxyhydroxide (Fig. 3) and a much slower cumulative release of leachable selenium (Fig. 4) with treatment. The total leachable selenium is considered to be 0.033 mmol.

The first point, at time = 0 weeks in Fig. 3 is the initial rinse of the material. The initial leaching of the untreated control yielded a large concentration of selenium compared to subsequent cycles. The initially released selenium had accumulated since exiting the coal preparation plant. The treated samples released very little selenium initially. The mean value and standard deviation of released selenium



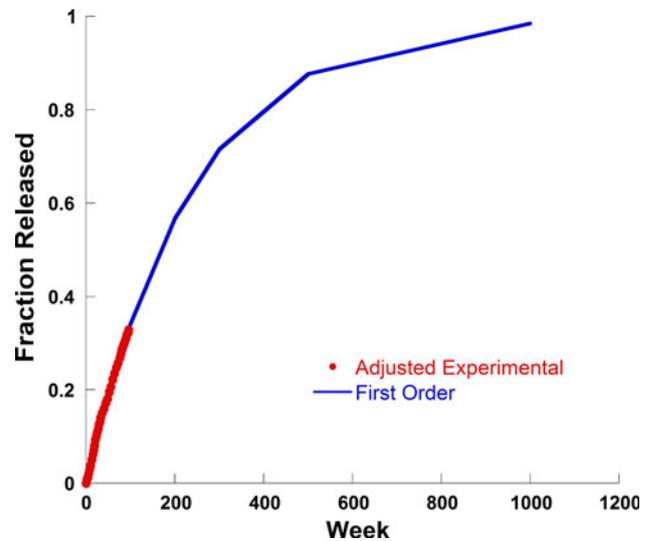
**Fig. 3** Concentration of selenium released during the discrete sampling over the 96 weeks for treated *filled square* and untreated *filled circle* tailings. The left ordinate is the actual concentration; the right ordinate multiplies the laboratory concentrations by the 6.4 factor to represent field concentrations



**Fig. 4** Cumulative percent released selenium by treated *filled square* and untreated *filled circle* cells referenced to 0.0033 mmol of releasable selenium in the tailings

from the first washing for the controls was  $5.9 \pm 3.5 \mu\text{g/L}$  (59%). The treated sample selenium concentrations at time = 0 were  $0.7 \pm 0.4 \mu\text{g/L}$  (57%). Each sample showed similar variability, but significantly different mean values.

The presumption, based on previous work with iron oxyhydroxides and selenite (Merrill et al. 1985; Su and Suarez 2001; Zhang and Sparks 1990) is that the selenium is permanently sequestered; this is not just a delayed

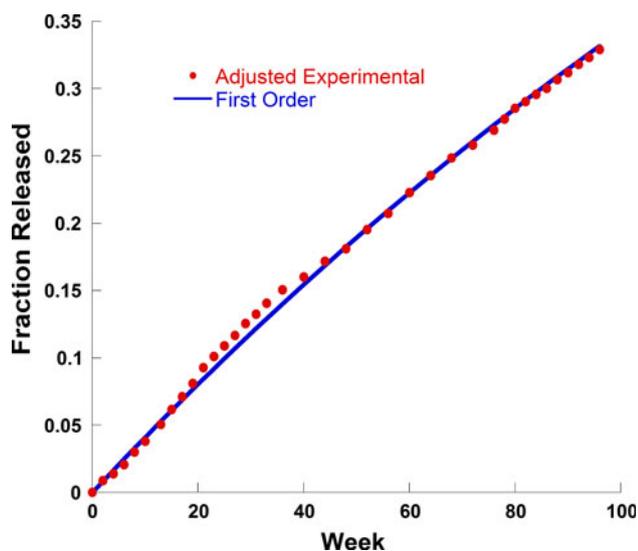


**Fig. 5** First order kinetic plot of selenium release from the controls. First rinse is not considered

release phenomenon. The capture of selenium by iron oxyhydroxide is demonstrated at time zero in Fig. 3, where the selenium that would have been released if the samples had been untreated ( $5.9 \mu\text{g/L}$ ) was not found.

The fraction of extractable selenium released from the control (Fig. 4) exceeds that released by the treated cells. The slope for the treated sample plot is 33% of the slope of the control. After 96 weeks, 35.1% of the extractable control selenium had been released and 11.6% of the selenium from the treated cells had been released. The release data for selenium from the controls was fit to a first order release (Fig. 5).

The evaluation is straightforward, but depends on the assumption that the selenium release rate is proportional to the selenium concentration in the solid, and that only one mechanism is responsible for selenium oxidation/mobilization. This assumption is chemically flawed, which is evident in the sequential extraction experiments where extractable selenium is recovered in increasing severe extraction solvents, but an average release rate can be expressed. Continuation of the cell experiment can shed light on this aspect. The first, uncontrolled data point was removed from the data set, such that only selenium released from rock and leached during the study was considered. In addition, the extractable selenium in the rock (using the 33% factor), not the total selenium content was evaluated. The rate constant used in Fig. 5 was  $0.0042 \text{ week}^{-1}$  (which is  $0.06\% \text{ day}^{-1}$ ). The full function was not plotted in Fig. 5. The experimental data and some points calculated using the function at longer times were used; hence, the flat portions of the curve. The fit of the first order equation (fully plotted) to the experimental points can be seen in Fig. 6.



**Fig. 6** Demonstration of fit of first order *plot* to experimental selenium data

Pumure et al. (2010) found selenium release rates to be rock dependent. They calculated a rate constant of  $0.034 \text{ min}^{-1}$  for their ultrasonic extraction of a shale. Comparing rate constants, the ultrasonic method released selenium over 80,000 times faster than the treatment cells. An ultrasonic extraction comparison using our southern tailings would be useful.

Figure 5 shows that roughly 600 weeks (almost 12 years) are necessary to remove 90% of the extractable selenium from the tailings by natural attenuation. The concentration of selenium after 600 weeks will be  $1.1 \text{ }\mu\text{g/L}$  when the field correction value of 6.4 is applied. Natural attenuation of the control to  $5 \text{ }\mu\text{g/L}$  selenium (field) discharge level requires that 64% of the selenium be released, which requires 245 weeks or 4.7 years.

The treated samples (Fig. 4) released selenium more slowly than the controls. This release was not fit to a first order equation since the release is a function of two processes, the intrinsic release as seen for the control and a separate adsorption process. The slope of the line in Fig. 4 for treated tailings is  $0.016\% \text{ day}^{-1}$ . In laboratory studies, selenite is removed quantitatively and quickly from solution by iron oxyhydroxides. The release profile seen in Fig. 4 is the result of a dynamic relationship between natural attenuation and permanent removal of selenium by iron oxyhydroxide. The iron oxyhydroxide becomes less effective over time. The decay of treatment performance needs to be evaluated experimentally. The convolution of the natural attenuation of the system, as shown in Fig. 5, and treatment at early times by iron oxyhydroxides will be required to determine the optimal dose.

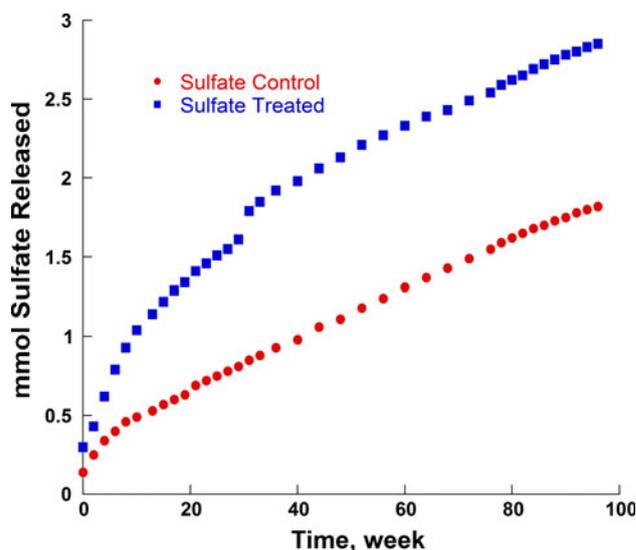
At longer times (after about 75 weeks), the efficiency of the treatment decreased, as seen by the increase in slope in

Fig. 4. Very little selenium (less than  $79 \text{ }\mu\text{g}$ ) was released over the course of the study with 75 g of iron treatment material added; the treatment material is not saturated with selenium. The loss of efficiency could be due to other deactivating reactions. An intriguing observation from Fig. 3 is the rather constant concentration of selenium in the leachate from the treated cells with time. The concentration released from the control cells tends to decrease, yet a reasonably constant concentration of selenium is measured from the treated cells. This suggests that the iron material captures all selenium over a base amount, or possibly some small percentage of the leached selenium is not in the form of selenite. Further work is needed to understand the long term behavior of the ameliorant.

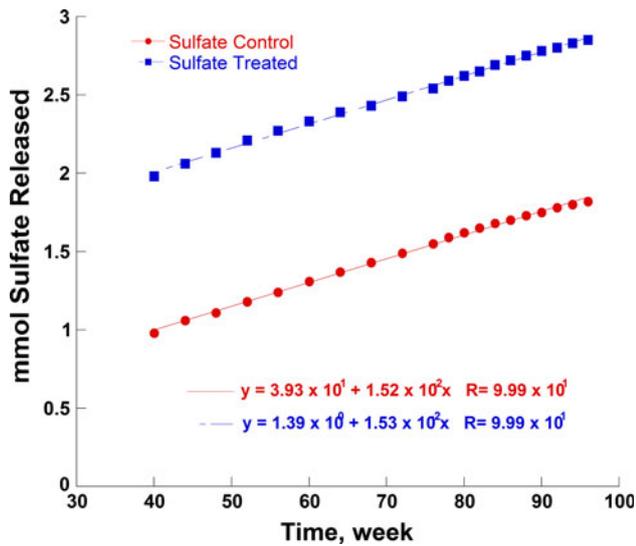
Sulfate

Sulfate release was greater in the cells with iron oxyhydroxide treatment (Fig. 7), but an expansion of the later stages of Fig. 7 (Fig. 8) shows equal slopes for treated and untreated sulfate production after 40 weeks with an offset of one mmol.

The added iron oxyhydroxide likely contained sulfate that was leached during the early stages of the study (Fig. 4), after which the treated cells begin to release sulfate at a rate equal to the controls (Fig. 5). The form of sulfate in the treatment material was not determined, but subsequent use of the same material in an unpublished field experiment has shown elevated calcium and sulfate for treated cells, implicating  $\text{CaSO}_4$ .



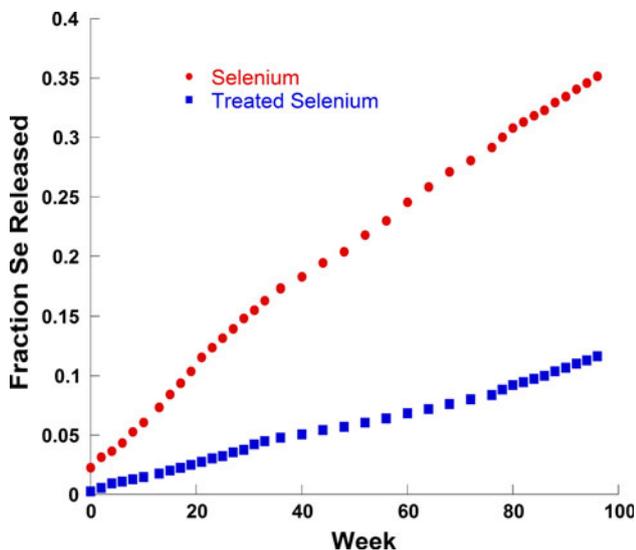
**Fig. 7** Cumulative sulfate released from treated *filled square* and untreated *filled circle* tailings over 96 weeks



**Fig. 8** Cumulative sulfate released from treated *filled square* and untreated *filled circle* tailings for the last 56 weeks. The derived equation lines are plotted

#### Leaching Rate: Selenium and Sulfur

The leaching rate of selenium was much higher than that of sulfur (Fig. 9). Table 2 summarizes the analyses of variance for the effects of element and time. Both were significant at the 95% confidence level. The results indicate that selenium leaching was more rapid than that of sulfur in the control cells. The time variable by itself was of little interest since it is expected with a cumulative parameter.



**Fig. 9** Elemental leaching rates of selenium and sulfur plotted over the 96 week period of the experiment. 'A' shows the leaching rates in the control cells while 'B' shows the leaching rates in the iron oxyhydroxide (FeOOH) treated cells

**Table 2** Analysis of variance (ANOVA) testing the null hypothesis that there was no significant difference in the cumulative % leaching rate as a function of either time (96 weeks of leaching) or element (selenium or sulfur)

Source of variation	SS	df	MS	F	P value	F crit
ANOVA control						
Time (weeks)	2.438	37	0.066	52.9*	7.6E-127	1.44
Element	0.791	1	0.791	634.3*	5.0E-83	3.87
Time × element	0.306	37	0.008	6.6*	8.5E-24	1.44
Error	0.474	380	0.001			
Total	4.008	455				
ANOVA FeOOH						
Time (weeks)	1.156	37	0.031	46.9*	7.7E-119	1.44
Element	1.792	1	1.792	2,691.3*	1.6E-174	3.87
Time × element	0.165	37	0.004	6.7*	5.1E-24	1.44
Error	0.253	380	0.001			
Total	3.365	455				

Single factors and the time × element interaction were tested. An asterisk following the *F* statistic indicates significance at the 95% confidence level. The *P*-value indicates the probability that there is no significant difference and *F*-crit indicates the minimum *F* value needed to disprove the null hypothesis. The *top half* of the table refers to untreated cells while the *bottom half* refers to cells treated with iron oxyhydroxide

More important was the time × element interaction. It was also significant that that the curves are not parallel and that the rate of selenium leaching was more rapid than that of sulfur.

In the iron oxyhydroxide treated cells, time, element, and the time × element interaction were also significant (Table 2). Sulfur leached at a higher rate from the iron oxyhydroxide treated cells (Fig. 9b), possibly due to gypsum in the iron oxyhydroxide.

Selenium and sulfur were released at significantly different rates from the tailings (Fig. 9). Both rates are referenced to the total rock content, not an assumed extractable fraction. Selenium released much faster than sulfur (its linear rate was 2.4 times faster). If selenium were homogeneously distributed in pyrite as a co-precipitant, and had the same chemical reactivity, it would be released at the same rate as sulfur. Vesper et al. (2008) found no correlation of selenium release to sulfur content in their extraction studies. Possible explanations are:

- (1) If selenium were homogeneously distributed in pyrite, it must react preferentially faster than sulfur and be more accessible. Notice (Fig. 9) that total selenium would be released before the total sulfur.
- (2) Selenium exists in concentrated pockets on the surface of pyrite, which allows preferential access and increased reactivity.

- (3) Selenium exists separately from pyrite, its release does not depend on pyrite reactions, and it exists primarily as  $Se^0$ , not selenide impurities in sulfide minerals.

The last possibility would account for the enhanced solubility of selenium in alkaline discharge systems versus acid systems. In alkaline systems, the acid from pyrite oxidation would be neutralized before the solution encountered selenium, increasing the possibility that a soluble form of selenium would be produced. The rate of pyrite oxidation would be incidental, since only the oxygenated, alkaline water would be necessary to dissolve  $Se^0$ . In acid systems, the pyrite-generated acid water would not be neutralized and when it encountered  $Se^0$ , dissolution would be thermodynamically discouraged (non-spontaneous). In the presence of an oxidizing agent,  $Se^0$  is thermodynamically favored to react to form selenite at alkaline pH.

No speciation was performed, but the efficiency of adsorptive removal observed in these experiments suggests that selenite is the main oxidation state. The resultant escaping selenium could be either selenate, as the result of partial full oxidation, or selenite that did not encounter the iron treatment material during leaching. The discharged selenium could also be particulate or colloidal  $Se^0$ . No detailed filtering experiments were conducted to affirm or eliminate this possibility.

#### Leaching Rate: Time and Treatment

The two-way analyses of variance indicated that, for both selenium and sulfur, the effects of time and treatment were significant at the 95% confidence level. The interactions of time and treatment were also significant. The leaching rate of selenium was significantly depressed by the addition of iron oxyhydroxide. Table 3 summarizes the analyses of variance for the effects of time and treatment on the selenium leaching rate. Both were significant at the 95% confidence level. Figure 4 plots the cumulative % selenium leached during the 96 week period of the experiment. The results indicate that about 33% of selenium leached from the control cells while only about 11% leached from the iron oxyhydroxide treated cells. The time × treatment interaction was also significant, indicating that the curves are not parallel and that the rate of selenium leaching was significantly retarded by iron oxyhydroxide application.

The sulfur leaching rate was also influenced by time, treatment, and the time × treatment interaction (Table 3). Sulfur leached at a significantly higher rate from the FeOOH treated cells (Fig. 7), possibly due to gypsum contamination of the iron oxyhydroxide.

**Table 3** Analysis of variance testing the null hypothesis that there was no significant difference in the cumulative % leaching as a function of either time (96 weeks of leaching) or treatment (control vs. FeOOH application)

Source of variation	SS	df	MS	F	P value	F crit
<b>ANOVA Selenium</b>						
Time (weeks)	1.970	37	0.053	38.5*	5.6E-106	1.4
Treatment	1.947	1	1.947	1,406.6*	8.6E-130	3.9
Time × treatment	0.505	37	0.014	9.9*	1.4E-36	1.4
Error	0.526	380	0.001			
Total	4.948	455				
<b>ANOVA Sulfur</b>						
Time (weeks)	1.524	37	0.041	77.9*	4.9E-154	1.4
Treatment	0.693	1	0.693	1,311.8*	2.7E-125	3.9
Time × treatment	0.064	37	0.002	3.3*	3.5E-09	1.4
Error	0.201	380	0.001			
Total	2.483	455				

Single factors and the time × treatment interaction were tested. An asterisk following the F statistic indicates significance at the 95% confidence level. The P-value indicates the probability that there is no significant difference and F-crit indicates the minimum F value needed to disprove the null hypothesis. The top half of the table refers to the selenium results while the bottom half refers to the sulfur results

#### Conclusions

Iron oxyhydroxide, when mixed with coal tailings, ameliorates selenium discharge. Reductions of up to 70% were achieved over 96 weeks. The results suggest that the initial form of selenium released from coal tailings is selenite, which is aggressively adsorbed by iron oxyhydroxides. The release of selenium from untreated tailings is about 0.06% per day and can be modeled by first order kinetics, which allows a prediction of the duration of release (in this case 4.7 years of selenium discharge above regulatory limits). This model does not consider longer term weathering processes that expose significant new surface area. The presence of iron oxyhydroxide treatment may shorten this time, but the length of treatment efficacy is not determinable from existing data.

No obvious relationship exists between sulfur and selenium release. Selenium is unlikely to be present in coal tailings solely as a selenide impurity of pyrite. The acidic condition generated by pyrite oxidation would favor release of elemental selenium, not metal selenides. However, the environmental mechanisms of oxidative dissolution of elemental selenium are not well studied.

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